RAI-342

WATER RECOVERY STUDY ...

ELECTROLYTIC PURIFICATION OF URINE

Contract NASw-520 with

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California

Report for the Period

July 7, 1964 to October 10, 1964

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FOREWORD

The work described in this report, "Water Recovery Study... Electrolytic Purification of Urine" under Contract NASw-520 with the National Aeronautics and Space Administration.

The authors wish to acknowledge the assistance of Messrs. Lawrence Sears, Arnold Katz, and Irving Lepelstat, laboratory technicians.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

1.0 SUMMARY ABSTRACT

Experiments leading to design parameters for a urine electrolysis module have been performed. These experiments indicate that intermittent operation of the electrodes or intermittent exposure of the urine to continuously operating electrodes yields the best current effciencies. Using a 3 min on - 6 min off cycle at 1.2 amps/cm^2 and 0.05 amps/ml, an 85% current efficiency has been obtained.

Two module designs are offered utilizing platinized platinum electrodes. The electrode arrangement envisioned places a Pt wire anode concentrically within a Pt perforated cylinder cathode, with a 0.2 cm annulus.

The preferred module design utilizes a centrifugal pump to circulate the urine within the electrolysis module. The module is comprised of an electrolysis chamber, a reaction chamber, a gas-liquid phase separator and of course a centrifugal pump.

When this module is operating at peak efficiency the electrolysis alone will consume 2.767 kilowatt-hours per six liter batch of average urine. The time required for this process is 7.73 hours. This is in comparison to 1.674 kilowatt-hours for the six hour process which is theoretically possible.

Analyses of the gases evolved during the electrolysis of real and "complex" synthetic urine show the CO_2/N_2 ratio anticipated for urea oxidation. They also indicate that real urine undergoes electrolytic oxidation less efficiently than the synthetic urine.

A coliform bacteria assay of raw urine and the same urine after electrolysis showed both to be essentially free of coliform bacteria.

2.0 INTRODUCTION

This report details the three month program to develop parameters for the design of a urine electrolysis module.

It had been previously demonstrated that it is possible to completely de-nitrify human urine by electrolytic means. This feat was accomplished, however, with only a 40-45% current efficiency. (See the report for the period September 7, 1962 to March 7, 1964 "Water Recovery Study" on Contract NASw-520.)

The basic motivation of this program then, was to study the electrolysis of urine from the standpoint of optimizing the current and energy efficiencies.

3.0 BACKGROUND DISCUSSION

Preliminary to any program to develop design parameters for the construction of the urine electrolysis module it is well to delineate the factors involved in the process.

Since it is desirable to minimize the power requirements for the process, one may delineate these factors as they affect the actual power requirements in comparison to the theoretical power requirement.

3.1 Theoretical Power Requirements

The theoretical power requirements may be calculated from the stoichiometry of the reactions and the composition of an average urine.

Average urine contains:

0.417 moles of urea/liter

and ca. 0.01 moles of other oxidizable organic species/liter.

The oxidation of urea by hypochlorite is represented by:

(1) $NH_2\ CONH_2 + 3OCl^- \longrightarrow CO_2 + 2H_2O + N_2 + 3Cl^-$

So it is seen that the oxidation of each mole of urea requires three moles of hypochlorite ion. The major components of the remaining organic species require ca. 11 moles of hypochlorite per mole. The total hypochlorite demand then is:

(2) $0.417 \times 3 = 1.251$

$0.01 \times 11 = \underline{0.11}$

1.361 moles OCl^-

The electrode reactions are:

anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

cathode: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

The reaction between chlorine gas and hydroxyl ion may be written as:

$$Cl_2 + 2OH^- \longrightarrow Cl^- + OCl^- + H_2O.$$

So it can be seen that each mole of hypochlorite produced requires the passage of 2 Faradays.

A liter of average urine then requires:

(5) 2F/mole x 1.361 moles/liter = 2.722 F/liter

Since a Faraday is equivalent to 26.81 ampere-hours, and the theoretical voltage of the hydrogen-chlorine cell is 1.728 volts, the theoretical energy requirement for the electrolysis is:

(6) 2.722 F x 1.728 V x 26.81 AH/F = 126 watt-hrs/liter

If it is assumed that the electrolysis is to require six hours, the power requirement is $\frac{126 \text{ watt-hrs/liter}}{6 \text{ hrs}}$ = 21.0 watts/liter.

3.2 Actual Power Requirements

Let us now consider the variables that effect the power consumption of the real process. For discussion purposes these may be broken down into two categories; those variables effecting the voltage requirements and those effecting the current efficiency. This breakdown is shown in Table 1.0.

3.2.1 Voltage Factors

3.2.1.1 pH

The voltage of the hydrogen electrode (the cathode) depends upon the pH as

(7) $E_H = -0.059 \times (pH)$

The voltage then becomes lower as the solution is made more acidic.

Acid conditions, however, do not favor hypochlorite formation. Slightly alkaline conditions are instead preferred.

Thus, the hydrogen electrode voltage under ideal conditions for hypochlorite formation then is in the area of,

(8) $E_H = (-)0.059 \times 8 = (-)0.472$ V

With real urine, the unadjusted pH is in the range of 5.0 - 6.0 pH units. The theoretical hydrogen electrode (cathode) voltage therefore will initially average $E_H = (-)0.59 \times 5.5 = -0.325$ V.

3.2.1.2 NaCl and Cl_2 Concentrations

3.2.1.2.1 The Effect on E_{Cl_2}

The effect the concentration of NaCl and dissolved Cl_2 have on the theoretical potential of the chlorine electrode (anode) are calculable via the following equation and assumptions.

(9) $E_{Cl_2} = (Eo)Cl_2 + 0.030 \log A_{Cl_2} - 0.059 \log A_{Cl^-}$

(1) where Eo = +1.358 V, the activity coefficients are equal to unity.

(2) Assume the initial Cl_2 concentration is $\approx$ .007 ppm. Since the solubility of Cl_2 is 7 gm/liter at 1 atmosphere of Cl_2 pressure, 0.007 ppm is in equilibrium with 10^{-6} atm. of Cl_2 gas.

The Cl^- activity in average urine is approximately 0.171N. Using the trace concentration figure of 0.007 g/liter as the initial concentration of Cl_2, we find that the theoretical initial chlorine electrode voltage is;

(10) $E_{Cl_2} = 1.358$ V + 0.03 log 10^{-6} - 0.059 log 0.171,

$E_{Cl_2} = 1.358 + [0.03 \times (-6)] - 0.059\ (-0.767)$

$E_{Cl_2} = 1.358 - 0.18 + (.059)\ (0.767)$

$E_{Cl_2} = 1.223$ V (for average urine)

After the cell is in operation for a finite time, especially at high current densities, the electrode will "see" essentially a saturated solution of Cl_2. The electrode potential can then rise to:

(11) $E'Cl_2 = + 1.358 + 0.045$

$E'Cl_2 = 1.403$ V

3.2.1.2.2 Solution Resistance and NaCl Concentration

The NaCl concentration and the specific resistance of real urine varies quite widely.

For a given electrode configuration and a given current density, the voltage drop due to the solution resistance will vary proportionally to the specific resistance.

3.2.1.3 Current Density

As has been indicated, the higher the current density for a given electrode configuration and a given urine, the higher will be the power requirement due to increased solution IR drop and polarization. Further, as has also been indicated, the theoretical anode potential is indirectly dependent upon the current density. Higher current densities producing higher dissolved chlorine gas concentrations.

3.2.1.4 Electrode Spacing

The effect of electrode spacing upon cell resistance is self evident in the equation for solution resistance, $R = \rho l/A$ where "l" is the distance between electrodes. Further, electrodes spaced too close may exhibit inordinately high resistances because of gas entrainment.

3.2.1.5 Temperature

Since the resistance of electrolytes decreases with increasing temperature, higher temperatures lead to lowered voltage requirements due to the lowered solution I-R drop.

3.2.2 Current Efficiency Factors

In discussing the factors that affect current efficiency we must consider not only the efficiency of hypochlorite production but also the factors that affect the reaction between hypochlorite and the organic species.

3.2.2.1 pH

The production of hypochlorite is most efficient under mildly alkaline conditions. Under these conditions there are an abundance of hydroxyl ions immediately available to react with all of the chlorine being generated at the anode.

3.2.2.2 Current Density

High current densitites, 0.1 to 1.0 amps/cm^2, are recommended for the production of hypochlorite.

3.2.2.3 Electrode Spacing

That electrode spacing is an important factor is readily demonstrated. Electrodes spaced extremely far apart (1 inch to 2 inches) yield essentially no hypochlorite formation as most of the chlorine gas generated escapes before it can react with the hydroxyl ions generated at the cathode.

Conversely, too close a spacing could lead to mixing of the chlorine gas from the anode with hydrogen from the cathode. This would result in production of HCl rather than production of HOCL.

3.2.2.4 Temperature

Moderately low temperatures favor the formation of hypochlorite. Temperatures in the range of 50°C favor the formation of chlorate ion. High temperatures should however, favor the hypochlorite oxidation of urea, etc., through the lowering of the solubility of CO_2 and other product gases.

3.2.3 Turbulence

In general, agitation tends to lower the efficiency of hypochlorite production, as it sweeps hypochlorite ions past the cathode where they can be reduced by atomic hydrogen.

The overall efficiency, on the other hand, from the point of view of the oxidation of the organic components of urine, should be aided by vigorous mixing.

3.2.3.1 Reaction Rates

Unless the reactions between the hypochlorite ion and the organic components are instantaneous, any process in which current is continuously supplied, will be inefficient. Hypochlorite not immediately consumed in the oxidation of urea, etc., will be available for the electrolytic conversion to the ineffective chlorate ion. This can be alleviated by intermittent operation of the cell or by intermittent exposure of urine to the electrodes in a circulating system. In this manner, sufficient time can be allowed for the hypochlorite formed to react completely with the organic species.

The reaction should also be speeded up by utilizing the "break-point" condition. That is, there exists an optimum concentration ratio of hypochlorite to reductant, at which the oxidation reaction proceeds most rapidly, this ratio is called the "break-point". These conditions can be maintained by adding the urine slowly to the electrode chamber which initially contains a salt solution. If, prior to adding any urine, a current is passed for a predetermined time a selected hypochlorite concentration may be established. If the urine is then added at a rate such that the consumption of hypochlorite equals the formation of hypochlorite, the desired hypochlorite concentration may be maintained.

In the continuous process, poor efficiency may arise from too slow a urine addition rate. If the urine is added too slowly, the excess hypochlorite is available for conversion to chlorate. If it is added too rapidly, on the other hand, one of course does not have sufficient hypochlorite available to oxidize all of the organic materials present even if the cell efficiently produces hypochlorite.

4.0 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Study of the Variation in Salt Content in Representative Samples of Urine

The conductivity of various fresh urine samples collected among the male members of the staff at different times of the day were measured. The resistances and the sodium chloride concentration they represent are listed in Table 2.0.

4.1.1 Effect of NaCl Concentration Variation in Cell Voltage

4.1.1.1 Anode Voltage and Cell Voltage

As may be seen in Table 2.0 and Figure 2.0 the $[Cl^-]$ content of real urine can vary widely, at least ranging from 0.265 N to 0.140 N. This introduces variation in the theoretical anode voltage. Due to this chloride concentration variation the initial anode voltage may range from 1.228 to 1.212 V. The anode voltage after the cell has operated sufficiently long to produce an envelope of Cl_2 saturated solution around the anode will rise, and range from at least 1.392 V to 1.408 V.

With real urine the average theoretical cell potential at the high current densities (without pH adjustment) will be:

(12) $$E_{cell} = 1.403 - (-0.325)$$
$$= 1.728 \text{ V}$$

4.1.1.2 Solution I-R Drop and Cell Voltage

The percent variation in the solution I.R. drop due to the variation in NaCl concentration may be roughly estimated in the following manner.

(13) $$R = \rho \frac{1}{A}$$

(14) $$E = IR = I\rho\, 1/A = \rho k$$

Then from Table 2.0:

(15) $E_{lower} = k(0.492) = 34.3\%$ below average.

$E_{higher} = k(0.934) = 24.5\%$ above the average.

Assume that: (a) the 6 hour urine conversion rate is the required rate (b) the desired current density is 0.5 amp cm^2, and (c) the electrode spacing is 0.2 cm.

Then since 73.0 AH.liter is the required number of faradays:

(16) $\frac{73 \text{ AH}}{6 \text{ hrs}}$ = current required.

The electrode area (x) will be:

(17) $\frac{12.2 \text{ A}}{X} = 0.5 \text{ amp/cm}^2$

or $X = 24.4 \text{ cm}^2$

(18) and $\therefore E_{soln} = (\frac{.2}{24.4})(12.2)$

(19) $= E_{soln} = (\frac{1}{10})$

(20) $E_{soln_{min}} = 0.49(1/10) = 0.0492$ V

(21) $E_{soln_{aver}} = 0.750(1/10) = 0.075$ V

(22) $E_{soln_{max}} = 0.934(1/10) = 0.0934$ V

4.2 Electrode Materials and Polarization

Figure 1.0 shows a plot if I vs. E for two cells of widely variant configuration and of different materials (platinum and carbon using a NaCl solution of the approximate average concentration encountered in urine.

The intercepts on the voltage axis show that the operating voltage of both cells is on the order of 3.0 V. The effective polarization potential is then approximately 1.3 V for both

platinum and carbon electrodes. (Platinum, however, will be used in the electrolysis module because carbon electrodes are more fragile and also tend to flake-off during operation.)

If the cell were to operate at the working voltage of 3.0 V and assuming 100% current efficiency we find that the power requirement for the six hour rate is at best 36.5 watts per liter.

4.2.1 Depolarized Cathode

It should be possible to operate the cathode of the electrolysis cell as an oxygen depolarized electrode. This would be a porous electrode through which an oxygen stream would be passed at a rate just sufficient to combine with all atomic hydrogen produced at the electrode-electrolyte interface. The formation of a gas film on the electrode would thus be avoided and the electrode would not polarize.

The cell operating voltage may be reduced by upwards of one half of the polarization potential.

4.3 Investigation of the Effect of Inter-Electrode Spacing and Current Density on Cell Voltage

Using the variable spacing the cell shown in Figure 3.0, a study was made to determine if there are any abnormal voltage requirements due to gas entrainment when small inter-electrode spacings are employed.

The data shown graphically in Figure 4.0 were obtained during the electrolysis of a synthetic urine in the variable spacing cell.

No abnormalities were observed in the voltage-current density curves over the range of inter-electrode spacings studied.

4.3.1 Influence on Cell Design

The curves shown in Figure 4.0 corroborate the

intuitive conclusions that the power requirements are minimized when the cell spacings and current densities are minimized. The best current efficiencies obtained on this program were as will be seen in the following sections, obtained using a current density slightly greater than 1.0 amp/cm^2.

4.4 Early Urine Electrolyses Utilizing "Break-Point" Conditions

Early experiments utilizing the continuous addition "break-point" cell (see Figure 5.0) gave results that were at the time extremely encouraging. See for example Figure 6.0.

Experiments in which the rates of addition were varied (see Table 3.0) indicated that there existed an optimum ratio of free chlorine concentration relative to oxidizable materials concentration at which the rate of oxidation would be maximized.

4.5 Study of the Effect of the Absolute Concentration and the Concentration Ratios of Hypochlorite and Urine Components Upon the Rate of Oxidation

To study these factors, a series of experiments was designed utilizing commercial bleach and a synthetic average urine containing urea, uric acid, creatinine and hippuric acid.

This series of experiments did not serve to disclose the optimum hypochlorite/urine ratio. It did however uncover a serious problem with the indo-phenol method of the nitrogen analyses.

4.5.1 The Unreliability of the Indo-Phenol Method of Nitrogen Analysis

The attempts to analyze the commercial bleach-synthetic urine mixtures revealed a basic problem with the indo-phenol nitrogen analysis. (For a description of the method see "Water Recovery Study", report dated April 15, 1965 - NASw-520.) It was found that the intensity of the color developed in the sample was a function of the

hypochlorite concentration of the sample as well as the urea-nitrogen concentration. The color intensity increased with increasing hypochlorite, resulting in erroneously high nitrogen analyses.

Further investigation showed the method to be sensitive to pH and also to depend upon the point at which the samples are diluted. This is because the analysis is designed to directly measure only very low-nitrogen concentrations. Nitrogen concentrations above this range result in the development of color intensities beyond the range of the Bausch & Lomb Colorimeter used in the analysis. It is necessary then to dilute the sample to the readable range. It had been standard practice to perform this dilution after the color development. This practice is now known to give erroneously low results. Dilutions must be made before the urease digestion is started.

The results in Table 3.0 and represented in 6.0 cannot be directly ruled out because of dilution errors as these particular analyses did not undergo any improper dilutions. They are however in doubt because no pH adjustments or hypochlorite concentration adjustments were considered.

It was thus necessary to change over to the Kjehldahl nitrogen analytical procedure.

4.5.2 The Kjehldahl Nitrogen Analysis

It is desirable to analyze samples of electrolyzed urine as quickly as possible after they are generated.

We selected the Fisher-Micro-Kjehldahl apparatus, and technique modified as described below.

4.5.2.1 General Procedure

The Kjehldahl method of analysis is useful for the determinations of all organic nitrogen other than nitro or nitroso nitrogen.

In essence, the process involves a catalyzed digestion with sulfuric acid which converts all organic nitrogen to ammonium sulfate via reaction (I).

$$\text{(I)}\quad \text{Org-N} + H_2SO_4 \xrightarrow[\text{Catalyst}]{CuSo_4} (NH_4)_2SO_4 + \text{etc.}$$

The ammonium sulfate is then converted to free ammonia and distilled from the basic reaction medium.

$$\text{(II)}\quad (NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

The ammonia distilled off is trapped in either dilute sulfuric or boric acids and is then either back titrated or directly titrated as the choice of trapping agent dictates.

4.5.2.2 Procedure and Apparatus as Modified

A 0.1 - 5.0 ml sample of the urea-containing solution is placed in a 100 ml flask and digested with 5 ml concentrated sulfuric acid by boiling gently in the presence of 3.5g K_2SO_4 and 50 mg $CuSO_4$. Three hours for digestion rather than the recommended 1/4 to 1 hour have been found to be necessary.

After digestion, the solution is cooled and 40 ml of distilled water added; the solution is then made basic by the addition of 20 ml of a 66% NaOH solution.

The liberated ammonia is then distilled to the collecting vessel which contains the ammonia trapping solution. The apparatus as purchased is provided with a steam generator to allow steam distillation of the ammonia. It was found that excessive condensation of moisture occurred in the top of the distilling flask and in the section of the apparatus leading to the condensor.

Ammonia held up in this condensate was causing low analytical results. Wrapping this portion of this apparatus with heating tape resulted in an improvement. Consistent, satisfactory

results, however, were not obtained until we resorted to a direct distillationin combination with the use of the heating tape.

The distilled ammonia is collected by trapping it in a 4% Boric acid solution. The ammonia content of this solution is then determined by direct titration with ca. 0.01N hydrochloric acid using the mixed indicator, bromocresol green - methyl red. This indicator gives a very sharp end point at(pH = 5.1).

4.6 Electrolysis of Real Urine Using the Continuous Addition "Break-Point" Method (Kjehldahl Analyses Used for Nitrogen Determination)

4.6.1 Extended Operation

A fresh sample of real urine was diluted with 0.2M NaCl to make a 10% urine solution. This solution was used as the feed stock for the operation of the electrolysis cell shown in Figure 5.0. As in all prior experiments with this cell, the electrode chamber was initially filled with 30 ml of 0.2M NaCl solution.

The current used was again 0.5 amp (0.5 amp/cm^2 in this case). The rate of addition of the feed stock was 60 ml/hr and a 5 ml sample was withdrawn every 5 minutes. The corresponding rate of addition of urine on a undiluted basis was therefore 6 ml/hr.

As indicated in Table 4.0 the feed stock N content was 1390 ppm N, or 13,900 ppm N on the undiluted basis.

Assuming a direct proportionality to the ampere hour requirements for average urine, one liter of this urine (undiluted) would require 80.9 ampere hours. Theoretically then at 0.5 amps, this cell should be capable of handling 6.18 ml of this particular urine per hour, if it were 100% efficient.

The actual rate of addition then was $\frac{6.0}{6.18}$ = 97% of theoretical.

The cell was operated at 0.5 amps, adding feedstock solution at 60 ml/hr (6.0 ml urine/hr) for 150 minutes removing 5 ml aliquots every 5 minutes.

The data listed in Table 4.0 were calculated in the following manner.

4.6.1.1 Calculation of the Maximum Possible Nitrogen Concentration in the Cell at any Time, Assuming Zero Cell Efficiency

The concentration of N in the cell after each addition has been made is calculated from:

$$C_{cell} = \frac{C_1 V_1 + C_2 V_2}{V_1 + V_2}$$

where C_1 = N concentration of the solution added

V_1 = volume of the solution added

C_2 = N concentration of the solution in the cell before the addition

V_2 = volume of the solution in the cell before the addition.

In our cell; at the start of the operation

$C_2 = 0$

$V_1 = 5$ ml

$V_2 = 30$ ml

and in this instance;

$C_1 = 1390$ ppm M.

The maximum possible N concentration of the first removed aliquot then is

$$C_{cell_{5\ min}} = \frac{C_1\ 5 + 0}{30 + 5} = 0.14\ C_1$$

After 10 minutes the maximum possible N concentration in the second aliquot sample removed:

$$C_{cell_{10min}} = \frac{C_1\ 5 + 30\overline{/0.14\ C_1} 7}{35} = 0.26\ C_1$$

Using this method, the concentration at each successive point is calculatable. This data is shown graphically in Figure 7.0.

4.6.1.2 Overall Cell Efficiency after 150 Minutes of Operation

From Figure 7.0 we see that at the 150 minute mark the maximum possible N content of the cell (zero efficiency) is 0.99 C_1.

In this particular case then this would be 0.99 x 1390 = 1376 ppm.

Since we are adding urine at 97% of the Theoretical Maximum addition rate, there should at no time be any nitrogen present in the cell, if it is 100% efficient.

The overall cell efficiency then is:

$$\frac{1376 - 840}{1376} = 38.95 \approx 39\%$$

4.6.1.3 Comments on the Experiment

It was predicted that operation of the continuous addition cell at less than theoretical rate of addition would prove inefficient.

This has been demonstrated by the fact that the overall cell efficiency dropped from 54% after ninety minutes to 39% after 100 minutes indicates that the use of addition rates even as high as 97% has a marked effect on cell efficiency after extended periods of operation.

4.7 The Batch-Wise Electrolysis of Real Urine Using the Intermittent Current Technique

A series of experiments, designed to determine if

there is (1) a benefit to be gained by intermittent cell operation and (2) if there is an optimum cycling regimen, were carried out. Table 5.0 tabulates the experimental conditions used and Figure 8.0 is a diagram of the cell.

The experimental data and calculated current efficiencies are tabulated in Table 6.0.

4.7.1 Calculation of Current Efficiencies

The experimental data in Table 6.0 were used to calculate the current efficiencies in the following manner.

Assume again that the ampere-hour requirement for the complete electrolytic conversion of a real batch of urine is directly proportional to that calculated for the average urine. Since this batch of urine had a nitrogen content of 13,010 ppm N the ampere-hours required per liter are 81.33 A.H./liter, or 4880 ampere minutes/liter. In this series of experiments 30 ml samples were employed. The theoretical number of ampere-minutes required for the 30 ml samples then is 146.4 a.m.

For each experiment, then the maximum possible percent decrease in nitrogen content then is:

$$(-) \quad N\%_{\text{Theoretical}} = \frac{\text{Actual amp min}}{146.4} \times 100$$

For example in experiment D of this series the maximum percent decrease in nitrogen content is from Table 6.0

$$(-) \quad N\%_{\text{Theoretical}} = \frac{131.5}{146.4} \text{ (amp min consumed)} = 89.8\%$$

The actual percent decrease in nitrogen however was from Table 6.0, 76.0%. The current efficiency of the cell then was:

$$\text{Current Efficiency} = \frac{N\% \text{ Actual}}{N\% \text{ Theoretical}} =$$

$$= \frac{76.0}{89.8} \times 100 = 84.5\% \approx 85\%$$

4.7.2 Comments

It is interesting to note that the better results, in terms of current efficiency were obtained when the "off" time was long relative to the "on" time.

This indicates that instantaneous oxidation of the organic components definitely does not occur.

It is likely that optimization of the current efficiency is possible thru further investigation of cycling regimens.

Table 7.0 lists some of the pH data recorded during experiments A, B, C and D. The cyclical variation of the pH seems to follow the production and consumption of NaOCl.

4.8 Complete Chemical Analyses and Bacteriological Assay of Raw and Electrolyzed Real Urine

A 60 ml sample of real urine (RAI Kjehldahl N = 13,050 ppm) was electrolyzed in the cell shown in Figure 8.0. In this cell, the volume of solution used results in exactly twice the exposed anode as was used in the experiments in Section 4.7. Thus, when 3.0 amps are supplied to the cell, the current density and current/ml urine are the same as in the experiments described in Table 5.0.

The cycling regime selected for the experiment was that of experiment D, Table 6.0. Upon the basis of the current efficiency of 85% observed in experiment D, Table 6.0 and the Kjehldahl N analysis of the urine batch used in this experiment, the calculated accumulated "on" time required to completely destroy the organic species in 60 ml of this urine at 3 amps is 115 minutes.

The cell was operated for a total accumulated "on" time of 147 minutes. This is 28% above the 115 minutes it was anticipated to require. The solution at 147 minutes was free of all detectable

odor other than chlorine and was the pale straw color of commercial NaOCl bleach.

It should be noted here that this run differed from experiment D, Table 5.0 in that it was necessary to shut the cell down overnight after the accumulation of 120 minutes of "on" time. Our initial Kjehldahl analysis showed a final N content of 0 ppm.

Consequently, samples of both the raw urine and the electrolyzed urine (147 min) were sent out for further chemical analyses, and samples of raw and electrolyzed urine were also sent out for a bacteriological assay, these results are shown in Table 8.0.

Repeat Kjehldahl analyses of the electrolyzed urine using considerably larger samples, however, showed a residual nitrogen content of 735 ppm.

This corresponds to a 94% decrease in N content, and a current efficiency of only 63%.

4.8.1 Comments on the Low Current Efficiency Obtained

The low current efficiency demonstrated in this experiment as compared to the 85% efficiency found in experiment D of Table 5.0 and 6.0 may be due to one or all of the following factors:

(a) the efficiency obtained may differ from urine sample to urine sample because of variations in the concentrations of minor components.

(b) The efficiency may well fall off as the concentration of oxidizable materials decreases.

(c) The overnight shut down period mentioned in Section 4.8 may have altered the efficiency but this does not appear too likely.

It would seem that (a) and (b) above are the most likely causes of the lowered efficiency. If (b) is the cause a

variable cycling regimen may be required to maintain high current efficiencies, utilizing briefer "on" periods and higher "off/on" ratios as the electrolysis progresses.

4.9 Collection and Analysis of the Gases Evolved During the Electrolysis of Urine, Real and Synthetic

Figure 9.0 is a diagram of the system used to collect the gases evolved during the electrolysis of urine.

The cell was operated using both real and synthetic urine. This experiment was performed prior to the series of experiments described in Section 4.7 and hence did not utilize intermittent operation.

The collection vessels had a volume of 250 ml. In order to ensure their being well swept of atmospheric gases the cell was loaded with a sufficient charge of urine to evolve approximately 2 liters of gas at S.T.P.

The cell was operated sufficiently long to generate 1.25 liters before the sample chamber was sealed. The gas samples collected from both real and synthetic urine were sent out for a mass-spectrographic analysis.

The data reported are presented in Table 9.0.

The data in Table 9.0 bear comment on several points.

(a) The immediate observation to be made is that the volume percent (i.e. mole %) of nitrogen is equal to the volume percent of carbon dioxide in both the real and the synthetic urine gas samples. This is as anticipated if the major source of these gases is urea.

(b) The ratio of $(CO_2 + N_2)/H_2$ is theoretically $0.834/1.361 = 0.613$.

The actual ratios found are:

Synthetic urine; $\frac{39.0}{59.0} = 0.661$

and real urine; $\frac{25.2}{62} = 0.471$

This would indicate, within experimental error, that 100% efficiency is obtained with the synthetic urine and approximately 75% efficiency was obtained with the real urine. This is in fair agreement with the efficiency obtained in experiment A of Tables 5.0 and 6.0.

(c) The presence of a greater amount of oxygen in the real urine gas sample is believed to be indicative of a lower utilization rate for the hypochlorite in the urea oxidation. This would result in a depletion of available chloride ion and result in the electrolysis of water.

(d) Although chlorine gas is readily detectable both by odor and the strong acidic reaction of moistened pH paper exposed to the anode gases, no free chlorine was found by mass spectrographic analysis.

(e) The higher volume of hydrocarbons, and the higher mass of these hydrocarbons, found in real urine gases is in line with anticipated results. The presence of organic compounds more complex than those in our synthetic is acknowledged and is indicated by the color, odor and foaming of real urine during electrolysis.

5.0 PRELIMINARY DESIGN SPECIFICATIONS FOR THE ELECTROLYSIS MODULE

Based on presently available information, specifications for a preliminary design of the electrolysis module have been made.

5.1 Materials

5.1.1 Electrodes

Platinized Platinum

5.1.2 Electrolysis Chamber and Associated Plumbing

Titanium

5.2 Design Parameters

5.2.1 Inter-electrode Spacing: 0.2 cm

5.2.2 Current Density: 1 amp/cm^2

5.2.3 Ratio of anode area/Solution Volume: 1.25 cm^2/30 ml

5.3 Electrolysis Process

The intermittent current process has been selected on the basis of the 85% current efficiency obtained.

5.3.1 Cycling Regimen: 3 min on 6 min off.

6.0 TENTATIVE MODULE DESIGNS

Based upon the preliminary design specifications two tentative urine electrolysis module designs for a four-man 6 liter/day system are offered. Both designs make use of the same electrode unit.

6.1 Electrode Configuration Common to All Module Designs

A platinized platinum wire 0.16 cm in diameter serves as the anode. This anode is arranged concentrically within a perforated platinized platinum cylindrical cathode whose i.d. is 0.56 cm and whose 0.d. is 0.58 cm.

Every 2.5 cm length of this concentric electrode assembly is assigned a urine volume of 30 ml. This meets specifications 5.2.1 and 5.2.3.

Figure 10.0 is a diagram of a 2.5 cm long electrode assembly segment.

6.2 Non-Circulating System

Figure 11.0 shows a diagram of an electrolysis system in which the electrolysis chamber holds the entire 6 liters of urine. In this system, the current cycling is achieved electronically, for example, by use of a square wave generator.

The ultra-violet lamp reactor shown in Figure 11.0 (and 13.0) is necessary to destroy any residual hypochlorite in the effluent stream. This step is used to avoid the development of dangerously high levels of NaOCl in the ultrafiltrand during the ultrafiltration.

The electrolysis chamber is a cylinder, whose inside dimensions are 15.65 cm diameter by 31.25 cm tall.

The chamber contains an array of sixteen electrode assemblies each 31.25 cm long spaced equally apart on the centers. See Figure 12.0.

6.2.1 Advantages of the System

The advantage to the system is that the pressure due to gases generated by the electrolysis and urea decomposition may possibly be used to empty the cell at the end of the electrolysis.

The same driving force would of course be utilized to force the electrolyzed urine through the gas-liquid phase separator, and into the ultrafiltration modules reservoir.

6.2.2 Disadvantages of the System

There are several disadvantages inherent to this system.

First of all, the system will have to operate under zero gravity. In order that the electrodes remain covered, there can be little or no free space in the electrolysis chamber to allow for the gas volume generated.

At an assumed cell temperature of 60°C the volume of gas evolved in the complete electrolysis of 6 liters of urine would be about 360 liters.

Allowing even a liter of free volume in the cell, the pressure developed would be at least 360 atmospheres (ca. 5,300 psi).

Not only does this pressure introduce a weight penalty due to the requisite strengthening of the chamber walls. It further not only makes sealing more of a problem but also raises the solubility of the gaseous products considerably. The effect this would have the reaction equilibrium is not completely known. Intuitively, however, one would expect this effect to be detrimental, certainly, the pH would be lowered.

In addition to the foregoing, it is not at all certain that gas pressure can be used to empty the cell under weightless conditions. Releasing the pressure on the liquid-gas-dissolved gas mixture may well result merely in expansion of the mixture as a foam.

6.3 Continuously Circulating System

Figure 13.0 is a diagram of a continuously circulating system. In this system current is supplied to the electrolysis chamber continuously. The urine, however, is exposed to the electrode only for part of the time. The volume of the electrode chamber is such that it represents one third the volume of the entire system. In the six liter module envisioned, the electrode chamber volume is 2 liters. The circulation rate necessary to achieve the 3min/6min regimen then is 40 liters/hr.

Thus, in this system, the urine flows through the electrode chamber at a rate such that each liter resides in the chamber for 3 minutes during which time hypochlorite is generated. The partially electrolyzed urine then flows into the reaction chamber where each liter resides for six minutes. In this chamber, the oxidation reactions are allowed to proceed. The urine and entrained gases then flow through the gas-liquid phase separator wherein the gases are bled off. At this point the de-gassed urine re-enters the electrolysis chamber for another cycle.

The electrolysis chamber in this system contains ten electrode assemblies each 16.67 cm long, spaced equally apart on the centers.

The inside dimensions of the cylindrical chamber are 16.67 cm in height by 12.36 cm diameter.

6.3.1 Advantages of the System

Since there is constant removal of the gases developed, the system will operate essentially at atmospheric pressure. Thus, the construction may be lightened and sealing becomes less of a problem.

Further, there will be no ill effects due to inordinate dissolution of CO_2 in the urine.

Additionally, but perhaps of minor importance, there is less of an expenditure required for electrodes then in the non-circulating system.

6.3.2 Disadvantages of the System

The major disadvantage of this system is the presence of the circulating pump.

In addition to the weight of the pump there is a penalty to be paid in the power required to run the pump motor.

6.4 Comparison of the Electrical Requirements of Both Systems. Exclusive of the Ultra-Violet Lamp

6.4.1 Non-Circulating System

6.4.1.1 Cell Current Per Pulse: 200 amps/pulse

6.4.1.2 Cell Voltage: 5.37 volts

6.4.1.3 Cell Power Requirements: 1,074 watts/pulse

6.4.1.4 Total Energy Required Per Average Six Liter Batch:

$$1.074 \times \frac{73.0 \text{ AH/liter} \times 6 \text{ liter}}{0.85 \text{ efficiency} \times 200 \text{ amp}}$$

$$= 2{,}767.1 \text{ watt-hours}$$

6.4.2 Continuously Circulating System

6.4.2.1 Cell Current: 66.67 amps

6.4.2.2 Cell Voltage: 5.37 volts

6.4.2.3 Cell Power Requirements: 358 watts (continuous)

6.4.2.4 Total Energy Required Per Average Six Liter Batch:

$$\frac{2{,}767.1}{\text{watts-hrs}}$$

6.4.2.5 Additional Energy Consumption by Pump: Not calculated

6.5 Recommended Module Design

It is the authors opinion that the continuously circulating system is the most promising. The continuous removal of evolved gases to avoid any pressure buildup is the most desirable feature of this system. Further, the use of a pump for liquid transfer seems the more reliable method under weightless conditions.

7.0 RECOMMENDATIONS FOR CONTINUED INVESTIGATIONS

7.1 Continued Investigation of Cycling Regimen

It is of course desirable to obtain even greater current efficiencies. Cycling regimens should be further optimized. The durations and the ratio of the durations of the on and off periods must be studied in more detail, as well as the desirability of using available cycle.

7.2 Current Densities and the Ratio, amp/ml

Concomittant with the continued study of cycling regimens should be the study of the effects of current density and the ratio, amps/ml. It is desirable to utilize the lowest current densities possible from the standpoint of lowering the voltage requirements, however, this factor is not independent but must be studied as a function of cycling regimens and the ratio, amps/ml.

The total time required for the electrolysis is a function of the current efficiency, the on/off time ratio of the cycling regimen, and the ratio, amp/ml. These parameters then, are limited in the number of values they may assume.by the maximum time available for the electrolysis.

The importance of obtaining reliable nitrogen analyses cannot be minimized. It is advisable in the future then to obtain replicate analyses.

TABLE 1.0

FACTORS DETERMINING POWER EFFICIENCIES

Voltage Factors

- pH
- NaCl and Cl_2 Concentrations
- Electrode Materials and Polarization Effects
- Current Density
- Electrode Spacing
- Temperature

Current Efficiency Factors

- pH
- Current Density
- Electrode Spacing
- Temperature
- Mixing or Turbulence
- Reaction Rates

TABLE 2.0

CONDUCTIVITY OF RANDOM URINE SAMPLES

Sample	R(ohms)	p(ohm-cm)	Normality of NaCl (Figure 2.0)
Urine (Two weeks old)	6.330	0.633	0.21
Fresh Urine	5.440	0.540	0.24
Electrolyzed Urine	5.900	0.590	0.22
Synthetic Urine	6.820	0.682	0.19
Fresh Urine	8.330	.833	0.16
Fresh Urine	6.630	.663	0.19
Fresh Urine	5.20	.520	0.25
Fresh Urine	4.92	.492	0.27
Fresh Urine	9.34	.934	0.15
Fresh Urine	6.17	.617	0.22
Fresh Urine	7.46	.746	0.17
Fresh Urine	6.84	.684	0.18

TABLE 3.0

INDO-PHENOL ANALYSES FOR THE NITROGEN CONTENT OF ELECTROLYZED URINE-SALT SOLUTIONS USING VARIOUS RATES OF URINE ADDITION IN THE CONTINUOUS ADDITION "BREAK-POINT" METHOD

% of Theoretical Addition Rate	Time (min)	Urea Nitrogen in Solution (ppm)	Chlorine Concentration (ppm)
81	10	0.875	110
81	20	0.916	110
81	30	0.666	110
81	40	0.708	110
24	10	1.68	320
24	20	1.32	100
24	30	1.20	80
24	40	0.76	30
143	4	2.11	1
143	8	3.98	1
143	12	7.96	1
143	16	5.47	1

TABLE 4.0

EXTENDED RUN, CONTINUOUS ADDITION CELL

Sample	N Concentration in ppm			Cell Efficiency
	Calculated Maximum at Zero % Efficiency	Calculated Minimum at 100% Efficiency	Found	
Feed Stock	----	----	1,390 ppm	----
90 minute sample	1295	Zero	600 ppm	54%
150 minute sample	1376	Zero	840 ppm	39%

TABLE 5.0

CONDITIONS FOR CYCLING REGIMEN EXPERIMENTS

Experiments	(minute)	Total Accumulated "on" Time	Current amps	Current Density amps/cm^2	Maximum Cell Temperature
A	90 on zero off	91 min	1.5	1.2	89°C
B	5 on 5 off	95 min	1.5	1.2	80°C
C	15 on 15 off	90 min	1.5	1.2	85°C
D	3 on 6 off	87 min	1.5	1.2	72°C

TABLE 6.0

CYCLING REGIMEN EXPERIMENTS; NITROGEN ANALYSES AND EFFICIENCIES

Experiment	Raw	Electrolyzed	ampere-min consumed	- $\triangle$N% Theoretical	Actual	Current Efficiency %
A	13010	5100	136.5	93.3%	60.8	65
B	13010	4665	142.5	97.4%	64.1	66
C	13010	3600	135.0	92.2%	72.3	78
D	13010	3123	131.5	89.8%	76.0	85
Ideal Conditions	13010	Zero	146.4	--	--	--

TABLE 7.0

CYCLICAL NATURE OF THE pH IN THE INTERMITTENT CURRENT EXPERIMENTS

Time of Reading	Experiment B	Experiment C	Experiment D
End of First "On" Period	9.0	7.0	8.0
End of First "Off" Period	7.0	6.5	7.6
End of Mid-Point "On" Period	7.2	7.2	8.1
End of Mid-Point "Off" Period	7.0	7.0	7.0
End of next to last "On" Period	7.2	7.2	7.1
End of last "Off" period	6.8	7.0	7.0

TABLE 8.0

CHEMICAL ANALYSES* AND BACTERIOLOGICAL ASSAYS;** RAW AND ELECTROLYZED URINE

Sample	N(RAI)	(Cl^-)	(Ol^-)	(NO_3^-)	(NO_2^-)	(CO_3^-)	S	C	Solids %	Coliform Bacteria
Raw	13,050 ppm	7,100 ppm	Zero	302 ppm combined		4,680 ppm	820 ppm	1.97%	4.41	<1/cc
Electrolyzed	735 ppm	3,830 ppm	19 ppm (2 week old sample)	84 ppm Zero		Zero	330 ppm	0.48%	2.43	<1/cc

*The chemical analyses, except N) were provided by Schwarzkopf Micro Analytical Laboratories, Woodside, New York.

**The bacteriological assays were provided by: Food and Drug Research Laboratories, Inc. Maspeth, New York.

TABLE 9.0

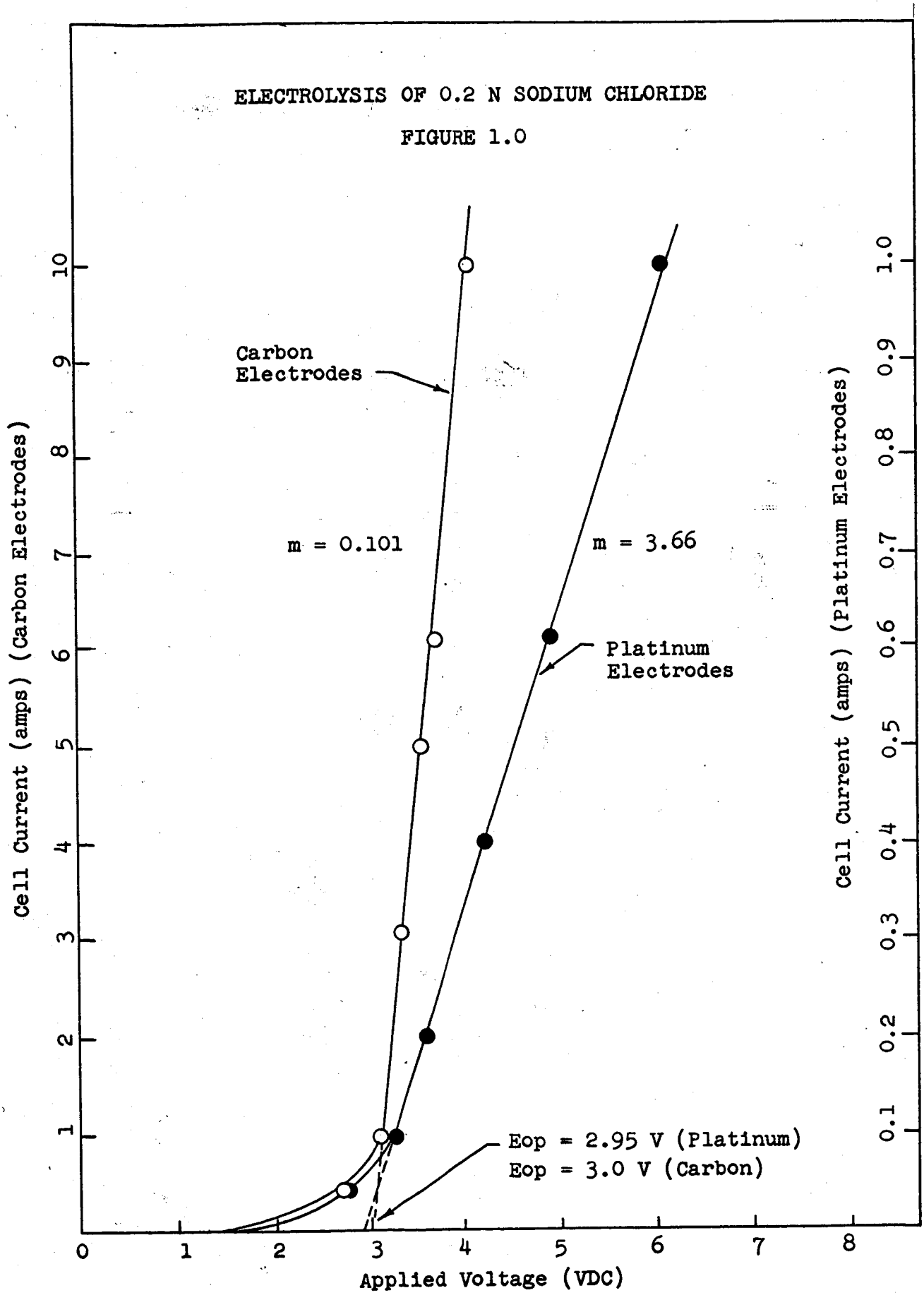
COMPOSITION OF GASES EVOLVED DURING URINE ELECTROLYSIS

Constituents	Synthetic Urine	Real Urine
	Concentration % Volume/Volume*	
Nitrogen	19.5	14.7
Oxygen	1.92	8.17
Argon	.067	.10
Carbon Dioxide	19.5	14.5
Hydrogen	59	62
Hydrocarbon	.036**	.87***

*These mass spectrometric analyses were performed by: Gollob Analytical Service, Inc., 47 Industrial Road Berkeley Heights, New Jersey.

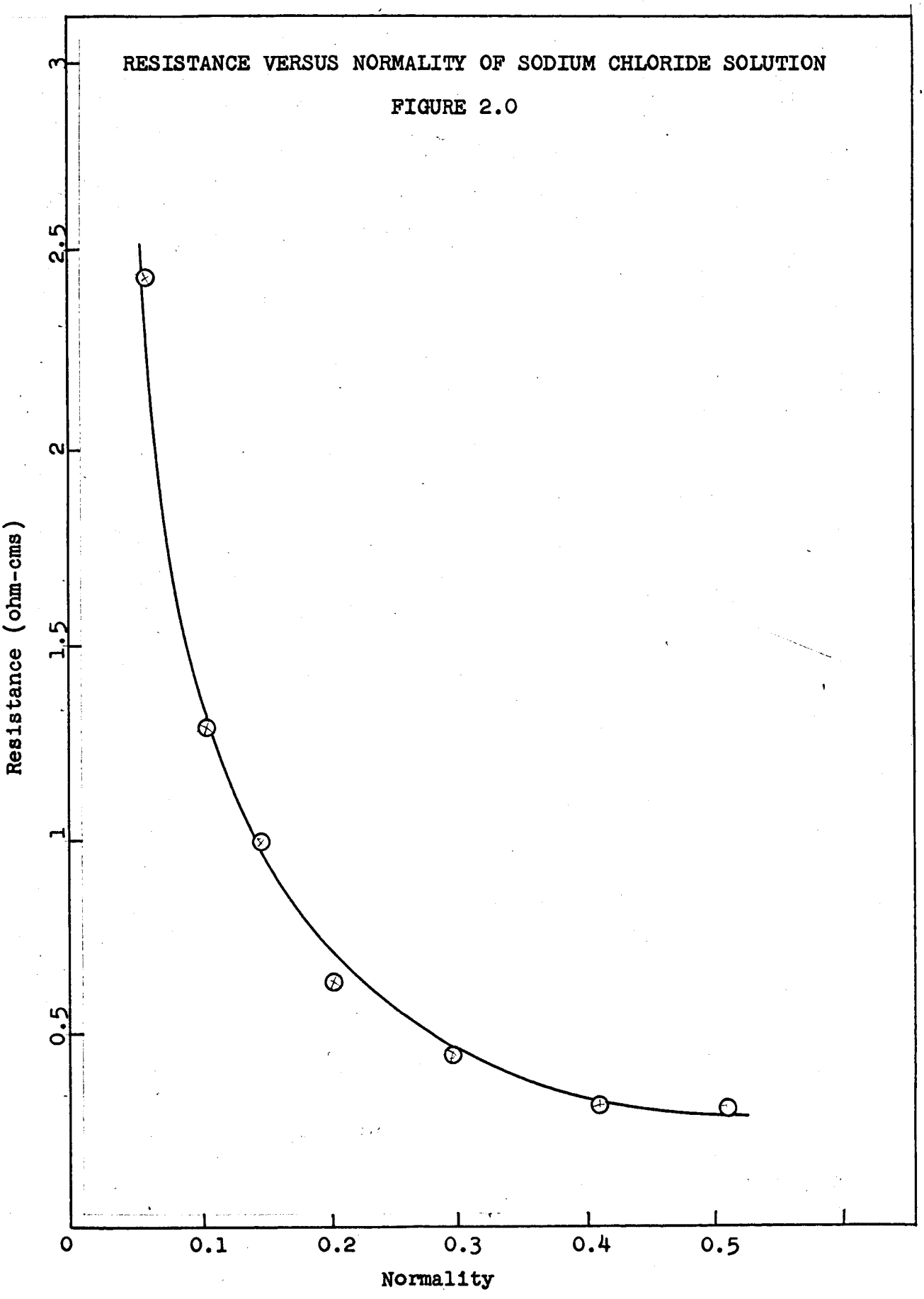
** Chlorinated hydrocarbon containing two chlorine atoms, major peaks at masses 61, 63, 81, and 83.

*** Chlorinated hydrocarbon with probably three chlorines and possibly a fluorine, major peaks at masses 116, 101, 86, 67, and 47.


ELECTROLYSIS OF 0.2 N SODIUM CHLORIDE
FIGURE 1.0
Carbon Electrodes
m = 0.101
m = 3.66
Platinum Electrodes
Eop = 2.95 V (Platinum)
Eop = 3.0 V (Carbon)
Cell Current (amps) (Carbon Electrodes)
Cell Current (amps) (Platinum Electrodes)
Applied Voltage (VDC)
0
1
2
3
4
5
6
7
8
1
2
3
4
5
6
7
8
9
10
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

RESISTANCE VERSUS NORMALITY OF SODIUM CHLORIDE SOLUTION

FIGURE 2.0



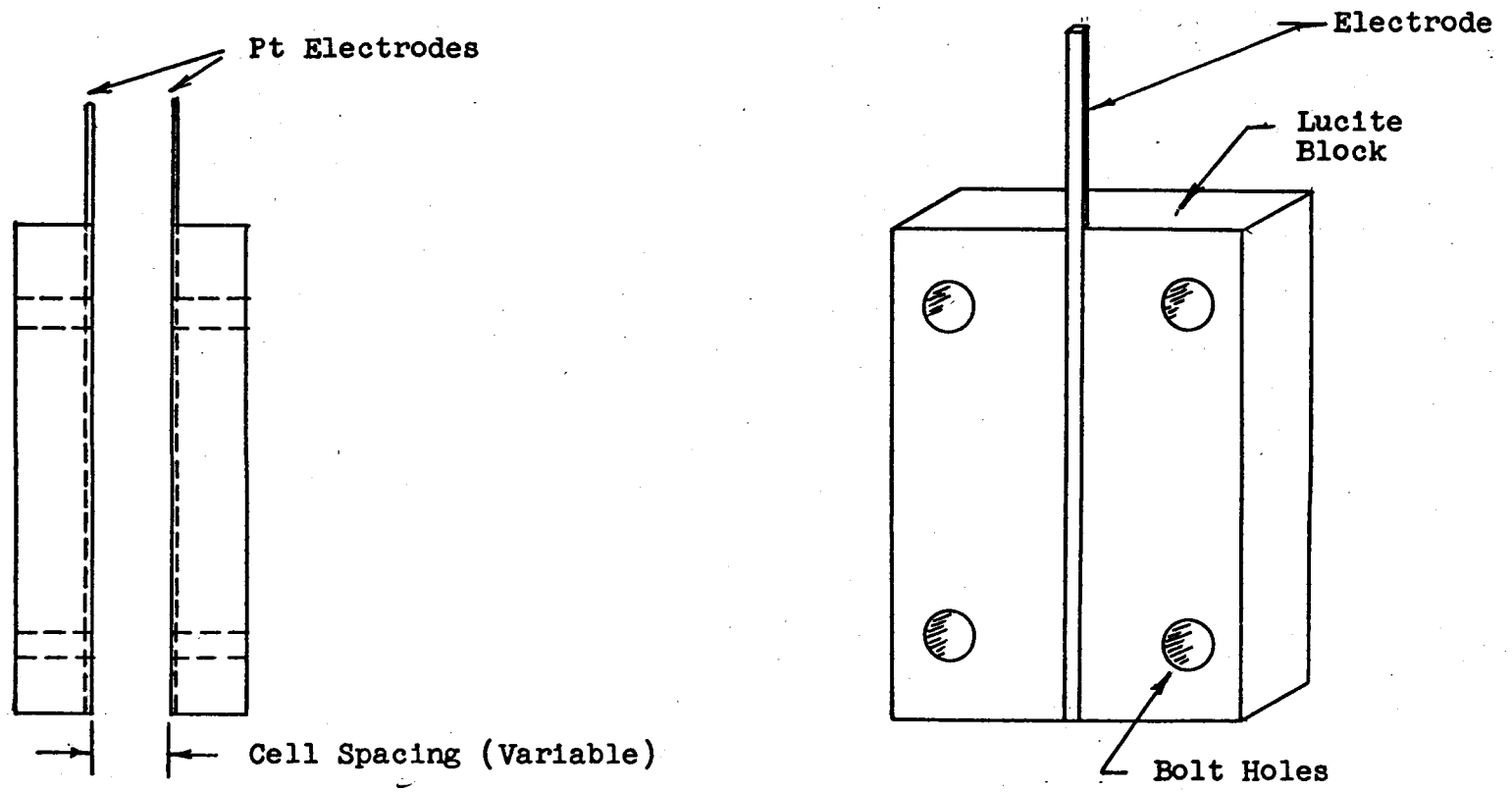
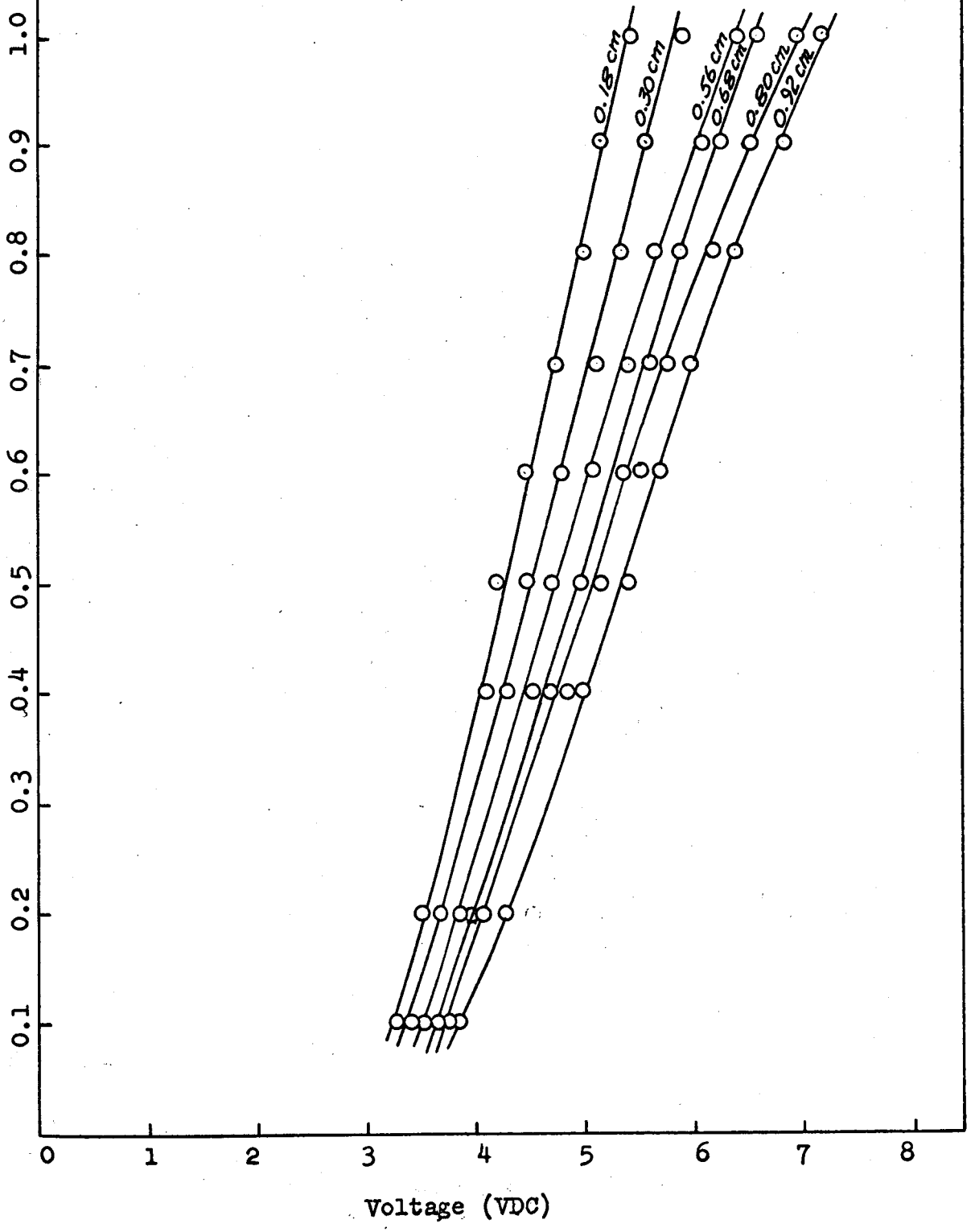


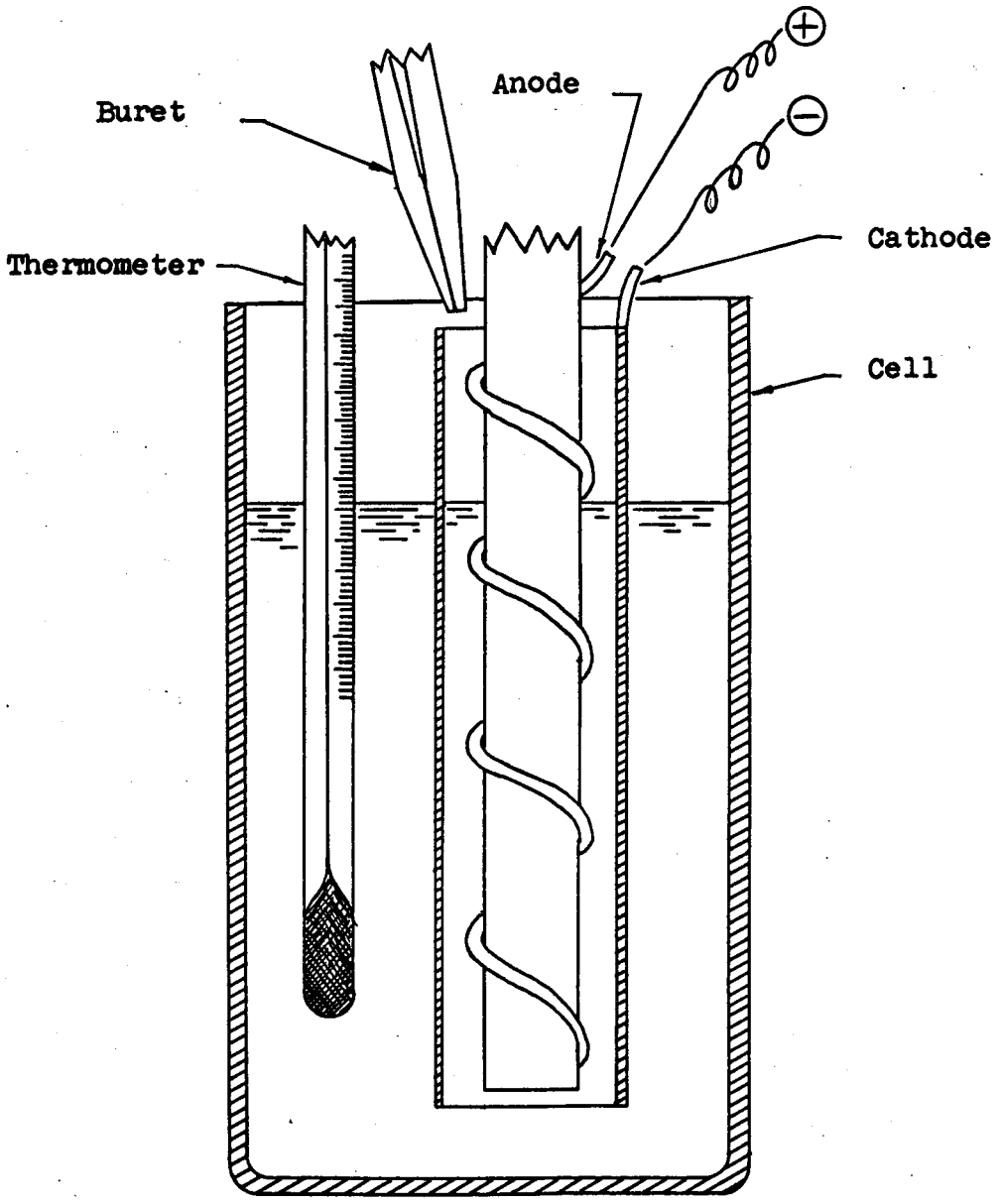
DIAGRAM OF CELL USED FOR CURRENT DENSITY - VOLTAGE MEASUREMENT

FIGURE 3.0

CURRENT DENSITY VERSUS VOLTAGE IN SYNTHETIC URINE SOLUTION WITH VARIOUS ELECTRODE SPACING

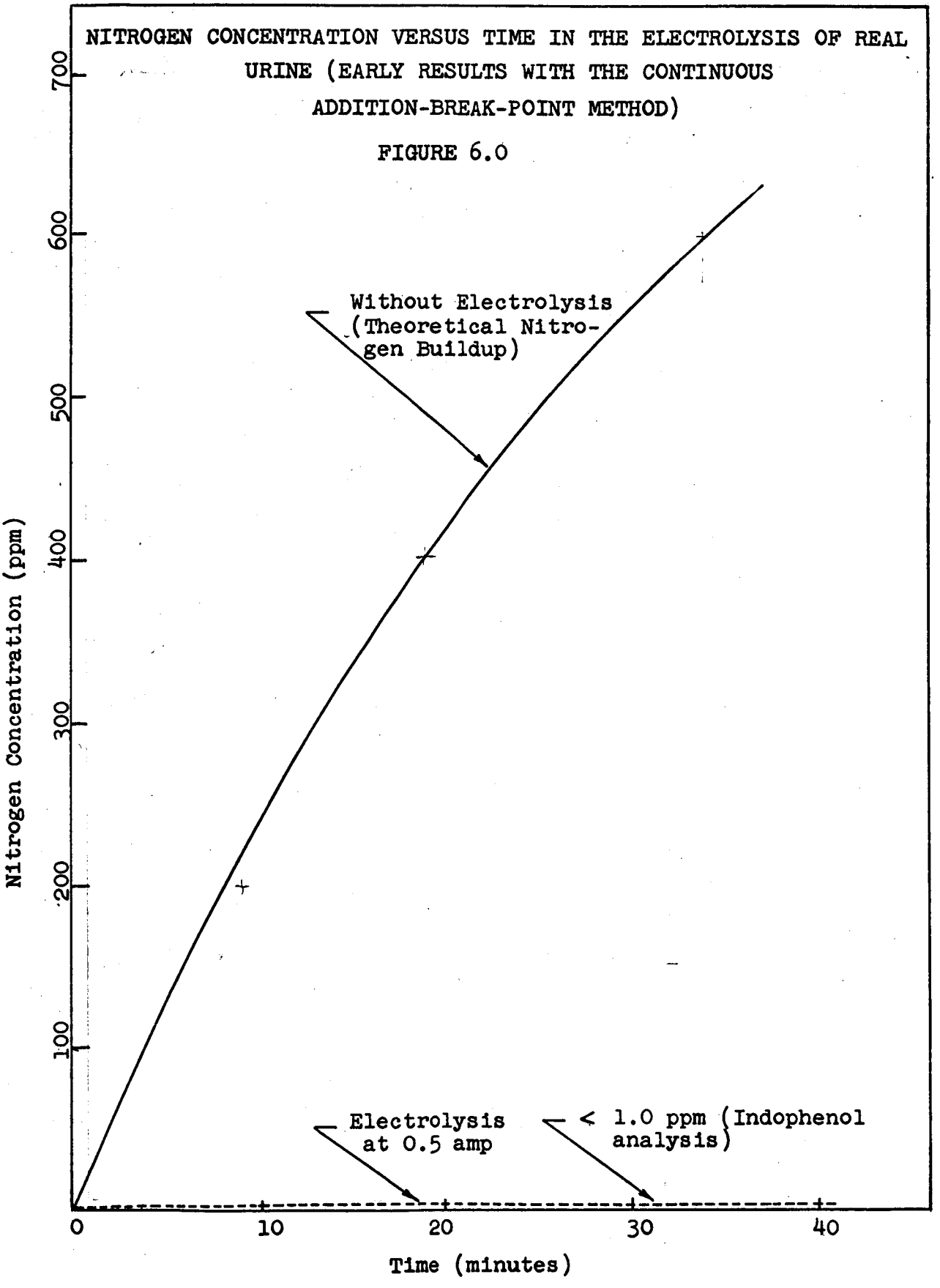
FIGURE 4.0





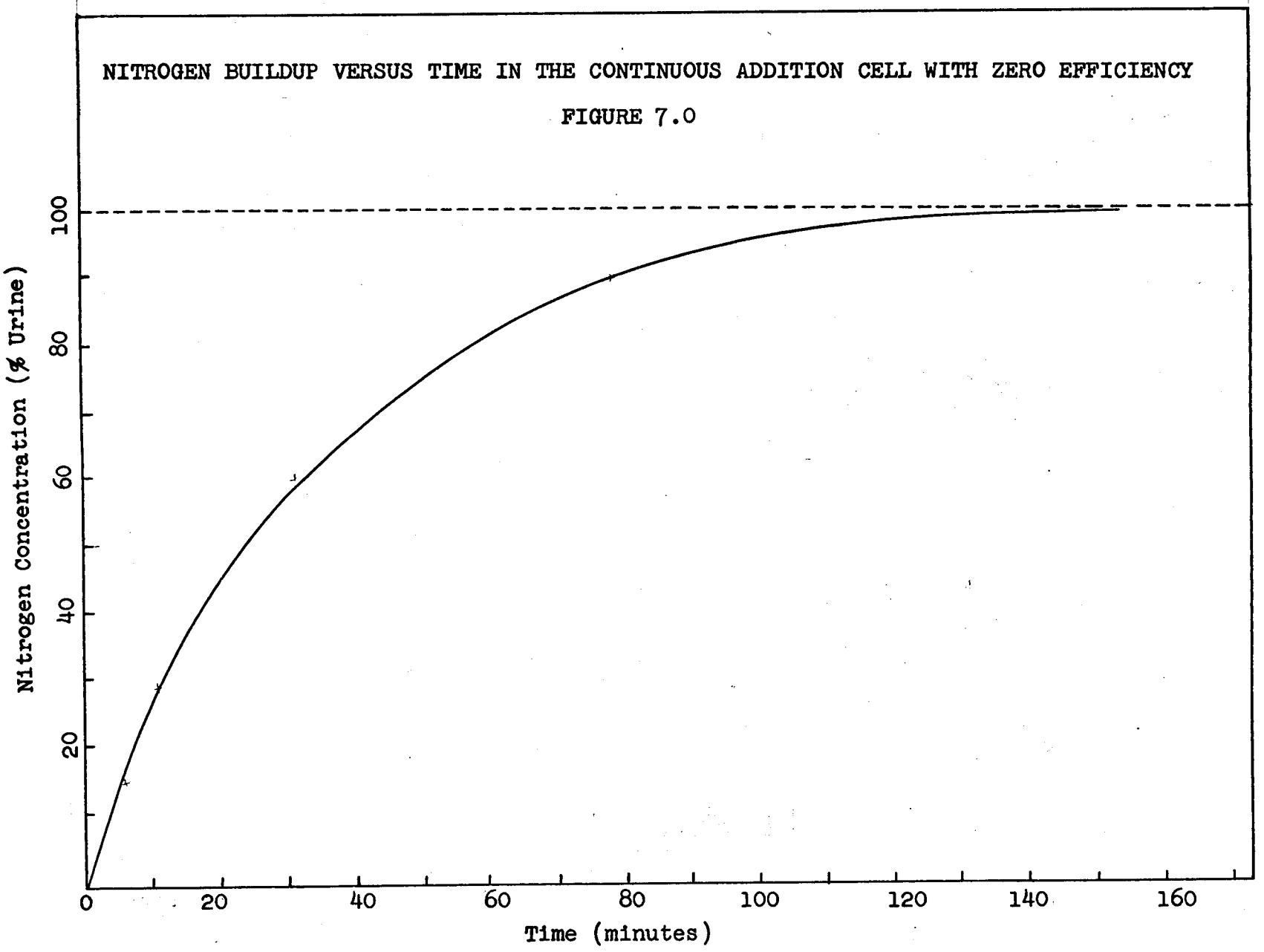
CONTINUOUS ELECTROLYSIS CELL

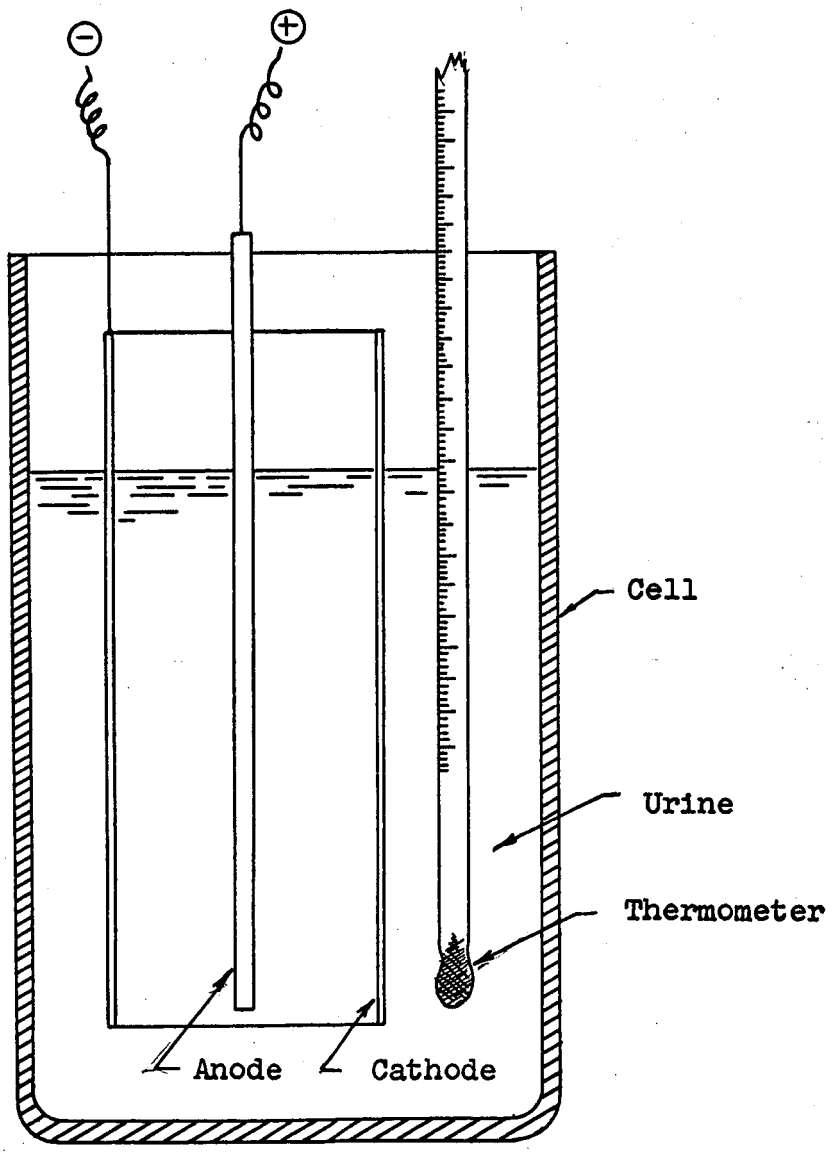
FIGURE 5.0


NITROGEN CONCENTRATION VERSUS TIME IN THE ELECTROLYSIS OF REAL URINE (EARLY RESULTS WITH THE CONTINUOUS ADDITION-BREAK-POINT METHOD)
FIGURE 6.0
Without Electrolysis (Theoretical Nitrogen Buildup)
Electrolysis at 0.5 amp
< 1.0 ppm (Indophenol analysis)
Nitrogen Concentration (ppm)
100
200
300
400
500
600
700
0
10
20
30
40
Time (minutes)

NITROGEN BUILDUP VERSUS TIME IN THE CONTINUOUS ADDITION CELL WITH ZERO EFFICIENCY

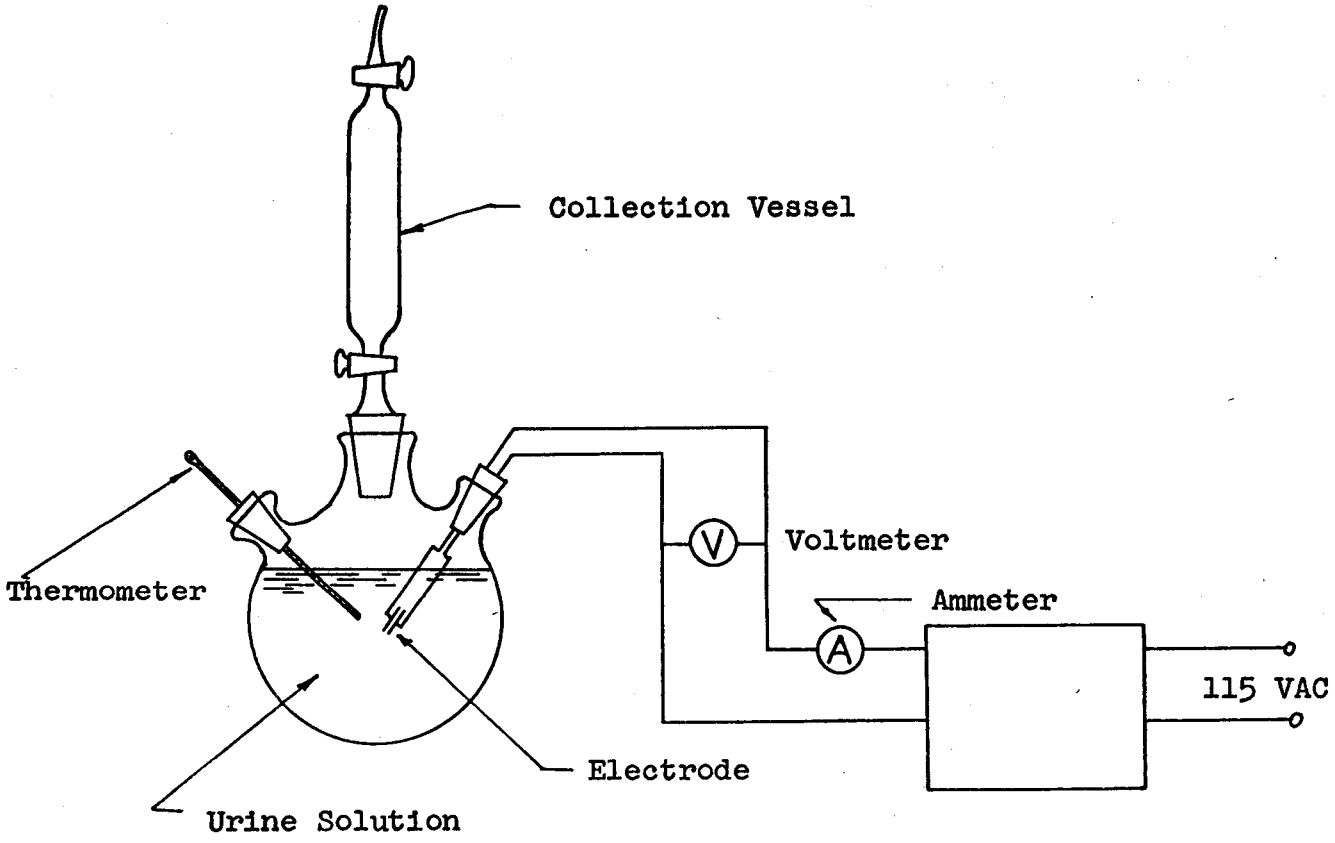
FIGURE 7.0





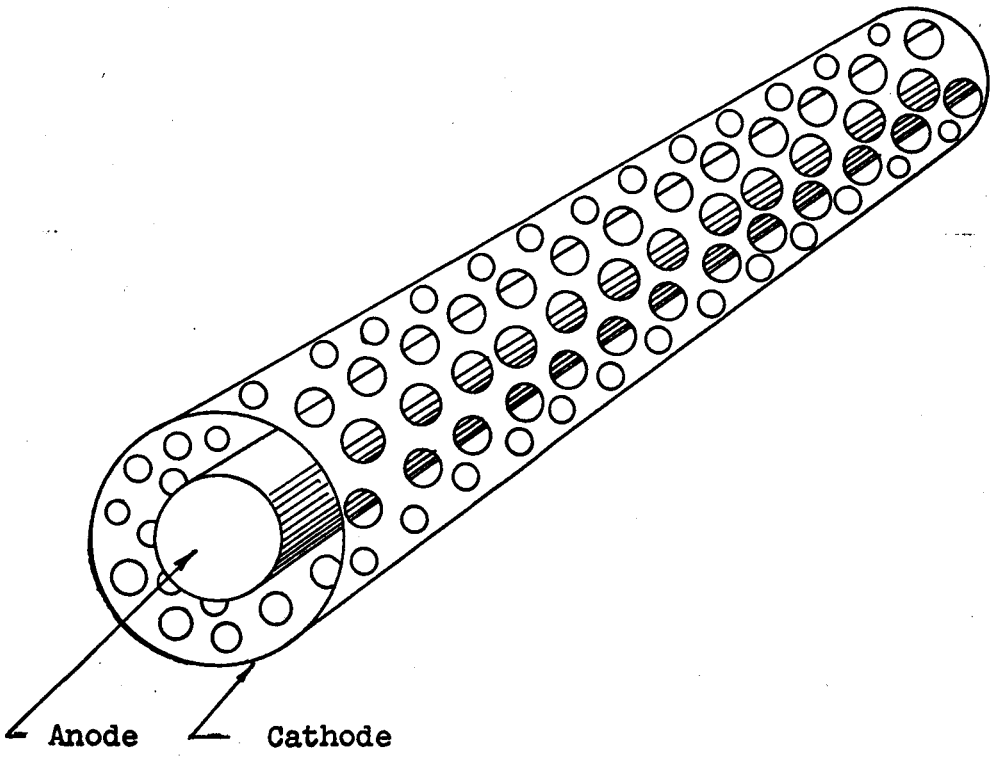
BATCH ELECTROLYSIS CELL

FIGURE 8.0



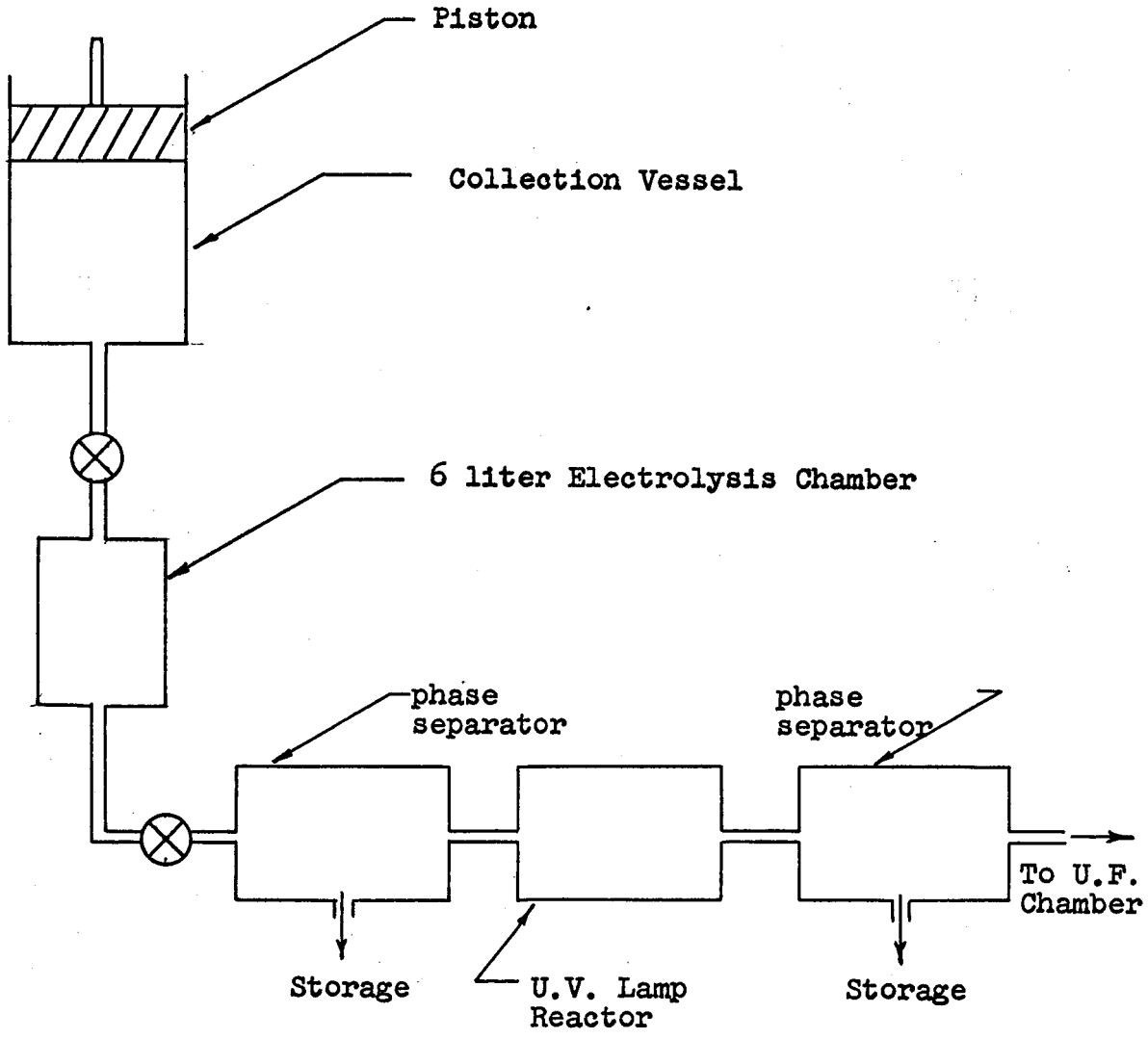
GAS COLLECTION APPARATUS

FIGURE 9.0



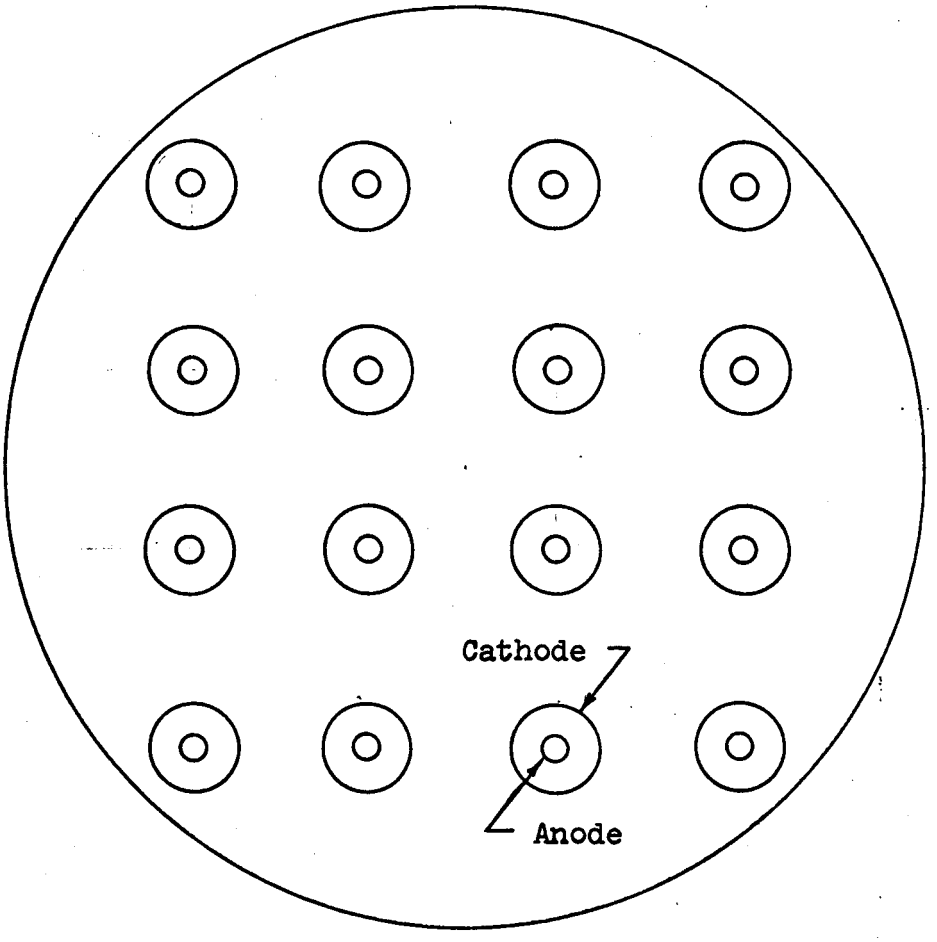
UNIT ELECTRODE CONFIGURATION FOR ELECTROLYSIS MODULE

FIGURE 10.0



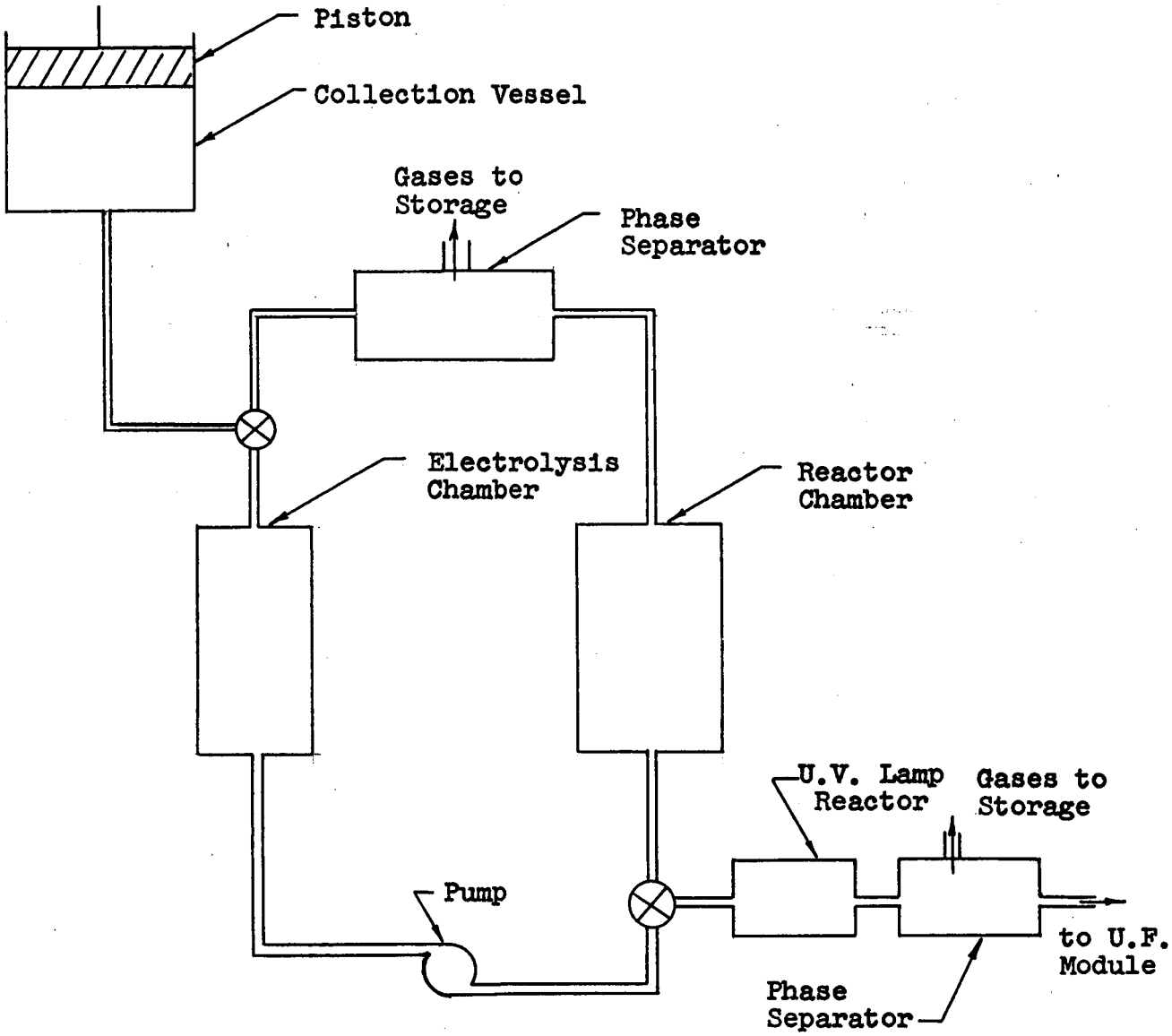
NON-CIRCULATING SYSTEM

FIGURE 11.0



ELECTROLYSIS CELL UTILIZING 16 ELECTRODE PAIRS
(END VIEW)

FIGURE 12.0



CONTINUOUSLY CIRCULATING ELECTROLYSIS SYSTEM

FIGURE 13.0

APPENDIX I

A. PHYSICAL AND CHEMICAL STANDARDS FOR DRINKING WATER

1946 United States Public Health Service Drinking Water Standards.

The elements and compounds listed may be present, but only to the maximum amount limited.

Turbidity	10 ppm (Silica scale)
Color	20 (platinum-cobalt scale or 15 chloroplatinate units)
pH	5.5-8.0
Solids	0.05%
Chloride ion	250 ppm
Copper	3.0 ppm
Ma nesium	125 ppm
Zinc	15 ppm
Sulfate ion	250 ppm
Phenolic Compounds	0.001 ppm as phenol
Iron and Manganese (together)	0.3 ppm

B. BACTERIOLOGIC REQUIREMENTS FOR DRINKING WATER

(United States Public Health Service and American Public Health Association Standard)

The accepted standard for coliform bacteria is a maximum of 2.2 coliforms per 100 ml, the preferred standard is zero colioforms. This standard is considered to be met when five 10 ml portions of water are examined by the fermentation tube method and gas is found in none of the five tubes.

Presumptive Test for E. Coli

Add five 10-ml portions of water to five 10 ml portions of double strength Standard Methods Lactose Broth (No. B4, dehydrated), or lauryl tryptose broth in fermentation tubes.

If water is suspected of being polluted, make higher dilutions and add five 1-ml portions of each dilution to five 10 ml of single strength Standard Methods Lactose Broth, so that negative results will be obtained in the highest dilutions.

Incubate all tubes at 35°C ± 0.5°C.

The presence of fermentation with gas in these tubes within 24 (±2) hours is presumptive evidence of the presence of Coliform organisms and is a "Positive Presumptive Test."

If no gas is formed in 24 (±) hours, continue the incubation to 48 (±3) hours. If fermentation with gas is present in any quantity at the end of the second, but not the first, 24 hour period, the test is considered as doubtful and the presence of Coliform organisms should be confirmed by the use of Standard Methods brilliant green lactose bile broth, endo medium or eosin methylene blue agar plates.

It is desirable that the tubes in which any gas found in 24 ($\pm$2) hours or 48 ($\pm$3) hours be subjected to confirmatory tests.

Absence of gas formation after 48 hours incubation at 25 to 37°C constitutes a negative test which requires no further confirmation.

A second standard method for determining the Coliform group is the membrane filter technique. This is a direct count method.

The procedure is described below.

(a) Duplicate 100 - 500 ml volumes of the test water are used.

(b) These are vacuum (or pressure) filtered under sterile conditions through autoclaved filter membranes. Pore size 0.05 to 0.45 microns.

(c) The membrane filters are placed right side up upon previously prepared absorbent pads wetted with culture media. (Endo agar or eosin methylene blue agar is recommended.)

(d) These are the incubated 20 $\pm$ 2 hrs at 35°C $\pm$ 0.5°C at 100% R-H. The samples are in an inverted position.

(e) The upper membrane surfaces are then examined for the dark purplish-green metallic appearing coliform colonies. A wide field microscope with a magnification of 10-15 diameters is used.